

**Refinement**Refinement on  $F^2$  $R = 0.035$  $wR = 0.045$  $S = 0.90$ 

2742 reflections

211 parameters

H atoms constrained

 $w = 1/[\sigma(F^2) + (0.02F)^2 + 0.6]$  $(\Delta/\sigma)_{\max} < 0.01$  $\Delta\rho_{\max} = 0.25 \text{ e } \text{Å}^{-3}$  $\Delta\rho_{\min} = -0.41 \text{ e } \text{Å}^{-3}$ 

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)Table 1. Selected geometric parameters ( $\text{Å}$ ,  $^\circ$ )

C11—C1	1.731 (2)	N2—C8	1.308 (2)
S1—C8	1.734 (2)	N3—C8	1.346 (2)
S1—C10	1.772 (2)	N3—C9	1.399 (2)
O1—C9	1.199 (3)	C6—C7	1.475 (2)
N1—N3	1.374 (2)	C9—C10	1.491 (3)
N1—C7	1.321 (2)	C10—C11	1.339 (2)
N2—C7	1.393 (2)	C11—C12	1.453 (3)
C8—S1—C10	89.60 (8)	N3—C9—C10	107.0 (2)
N3—N1—C7	101.3 (1)	S1—C10—C9	112.1 (1)
C7—N2—C8	101.7 (1)	C9—C10—C11	120.0 (2)
N1—N3—C8	110.1 (1)	C10—C11—C12	131.3 (2)
C8—N3—C9	117.7 (1)	C12—C11—H11	114.5 (2)
C11—C1—C6	122.2 (1)	C11—C12—C13	118.2 (2)
S1—C8—N3	113.6 (1)	C11—C12—C17	123.9 (2)
O1—C9—C10	128.2 (2)	C12—C13—H13	119.6
N3—N1—C7—C6	177.5 (2)	S1—C10—C11—C12	-2.4 (4)
C1—C6—C7—N2	-165.6 (2)	C10—C11—C12—C13	172.2 (3)

Table 2. Hydrogen-bonding geometry ( $\text{Å}$ ,  $^\circ$ )

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C5—H5 $\cdots$ N2	0.94	2.44	2.815 (2)	104
C11—H11 $\cdots$ O1	0.93	2.55	2.910 (2)	104
C17—H17 $\cdots$ S	0.95	2.50	3.218 (2)	133

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1993). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SIR* in *MolEN*. Program(s) used to refine structure: *LSFM* in *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *MolEN* (Fair, 1990) and *PARST* (Nardelli, 1995).

The authors acknowledge the purchase of the CAD-4 diffractometer under grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1204). Services for accessing these data are described at the back of the journal.

**References**

- Ali, M. I., Mostafa, A. B. & Soliman, A. A. (1976). *J. Prakt. Chem.* **318**, 12–18.
- Borbulevych, O. Ya., Shishkin, O. V., Desenko, S. M., Chernenko, V. N. & Orlov, V. D. (1998). *Acta Cryst.* **C54**, 442–444.
- Enraf–Nonius (1993). *CAD-4 EXPRESS*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.
- Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
- Gall, M., Hester, J. B., Rudzik, A. D. & Lahti, R. A. (1976). *J. Med. Chem.* **19**, 1057–1064.
- Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

- Kane, J. M., Baron, B. M., Dudley, M. W., Sorensen, S. M., Staeger, M. A. & Miller, F. P. (1990). *J. Med. Chem.* **33**, 2772–2777.
- Lagorce, J. F., Moulard, T. & Raby, C. (1992). *Arzneim. Forsch.* **42**, 314–318.
- Mir, I., Siddiqui, M. T. & Comrie, A. (1970). *Tetrahedron*, **26**, 5235–5238.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Prasad, A. R., Ramalingam, T., Rao, A. B., Diwan, P. V. & Sattur, P. B. (1989). *Eur. J. Med. Chem.* **24**, 199–201.
- Tozkoparan, B., Akgün, H., Ertan, M. & Rübsemann, K. (1995). *Arch. Pharm. (Weinheim)*, **328**, 169–173.
- Tozkoparan, B., Kılıçgil, A. G., Ertan, M., Kelicen, P. & Demirdamar, R. (1999). *Arzneim. Forsch. Drug Res.* In the press.
- Wang, Z., Bai, Z., Yang, J., Okamoto, K. & You, X. (1998). *Acta Cryst.* **C54**, 438–439.

*Acta Cryst.* (1999). **C55**, 1941–1943

## Configurational analysis of 14,14-dimethyl-12-oxatricyclo[9.2.1.0<sup>3,8</sup>]tetradeca-3,5,7-trien-13-one

REINHOLD ZIMMER,<sup>a</sup> GERNOT ZAHN,<sup>b</sup> FAIZ AHMED KHAN<sup>a</sup> AND HANS-ULRICH REISSIG<sup>a</sup>

<sup>a</sup>Institut für Organische Chemie, Technische Universität Dresden, D-01062 Dresden, Germany, and <sup>b</sup>Institut für Kristallographie und Festkörperphysik, Technische Universität Dresden, D-01062 Dresden, Germany. E-mail: zahn@physik.tu-dresden.de

(Received 26 March 1999; accepted 1 July 1999)

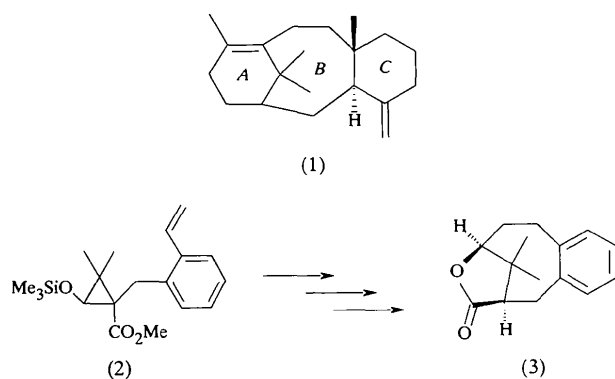
**Abstract**

The title compound,  $C_{15}H_{18}O_2$ , is shown to contain a *cis*-fused, five-membered lactone ring and bears some resemblance to the ring system of palitaxel (Taxol<sup>TM</sup>).

**Comment**

The taxane diterpenes are a group of substances isolated from various yew (*Taxus*) species that, with few exceptions, share the carbon skeleton (1) (Nicolaou *et al.*, 1994). A well known diterpene natural product containing this framework is Taxol (Wani *et al.*, 1971). Recently we described a practical procedure to construct the *BC*-ring system of the taxane framework by a novel reductive coupling reaction using samarium(II) diiodide (Khan *et al.*, 1997). As part of our current research program we are aiming at the subsequent formation of the *A* ring using the lactone moiety in key intermediate (3). Compound (3) was obtained in isomerically pure form, but the relative configuration of the stereocentres could not be determined unambiguously by NMR analysis. The X-ray analysis led to the determination of the structural features of (3) with the relative stereochemistry as

depicted. The title compound has a five-membered lactone ring *cis*-fused to a cyclooctane ring.



The asymmetric unit contains two independent molecules, (I) and (II) (Fig. 1). Both molecules have very similar bond lengths and angles. The conformations are slightly different which is reflected by different torsion angles (Table 1). The deviations from the ideal values (90, 180°) show that molecule (I) has small distortions at the bridgehead C4—C9 and (II) more at C19—C24—C25—C26.

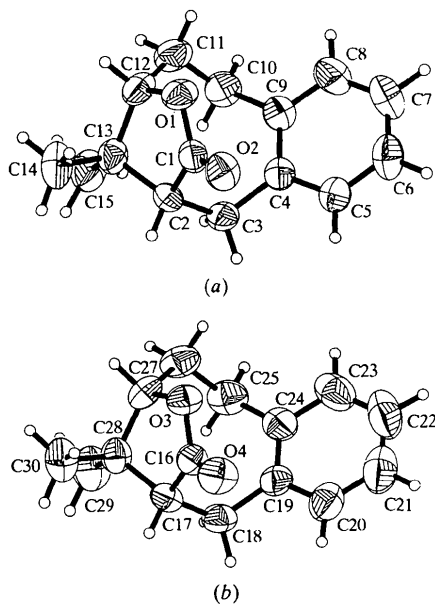


Fig. 1. Ellipsoid plots at the 50% probability level of (a) (I) and (b) (II).

## Experimental

The title compound (3) was prepared in a three-step reaction starting from methyl 1-(2-vinylbenzyl)-3,3-dimethyl-2-trimethylsilyloxycyclopropanecarboxylate, (2), as reported elsewhere (Khan *et al.*, 1997).

## Crystal data

C<sub>15</sub>H<sub>18</sub>O<sub>2</sub>  
*M<sub>r</sub>* = 230.29  
 Monoclinic  
*P*2<sub>1</sub>/*c*  
*a* = 10.7311 (7) Å  
*b* = 23.123 (2) Å  
*c* = 11.0657 (8) Å  
 $\beta$  = 112.043 (4)°  
*V* = 2545.1 (3) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.202 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

Mo *K*α radiation  
 $\lambda$  = 0.71073 Å  
 Cell parameters from 120 reflections  
 $\theta$  = 10.1–13.9°  
 $\mu$  = 0.078 mm<sup>-1</sup>  
*T* = 300 (2) K  
 Rectangular  
 1.06 × 0.87 × 0.36 mm  
 Colourless

## Data collection

Stoe Stadi-4 diffractometer  
 $\omega$ - $\theta$  scans  
 Absorption correction: none  
 5857 measured reflections  
 5571 independent reflections  
 3727 reflections with  
 $I > 2\sigma(I)$   
*R<sub>int</sub>* = 0.016

$\theta_{\max}$  = 27.02°  
 $h$  = -13 → 12  
 $k$  = -29 → 0  
 $l$  = 0 → 14  
 3 standard reflections  
 frequency: 120 min  
 intensity decay: none

## Refinement

Refinement on *F*<sup>2</sup>  
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.119$   
 $S = 1.138$   
 5571 reflections  
 452 parameters  
 All H-atom parameters  
 refined  
 $w = 1/[\sigma^2(F_o^2) + (0.033P)^2 + 0.66P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.15 \text{ e \AA}^{-3}$   
 Extinction correction:  
*SHELXL97* (Sheldrick,  
 1997a)  
 Extinction coefficient:  
 0.0133 (8)  
 Scattering factors from  
*International Tables for  
 Crystallography* (Vol. C)

Table 1. Selected torsion angles (°)

C5—C4—C9—C10	175.98 (19)
C4—C9—C10—C11	88.7 (3)
C20—C19—C24—C25	-179.38 (19)
C19—C24—C25—C26	84.8 (3)

Data collection: *STADIA* (Stoe & Cie, 1997). Cell refinement: *STADIA*. Data reduction: *XRED* (Stoe & Cie, 1996). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997b). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997a). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL97*.

We are grateful to Professor P. Paufler for making the four-circle diffractometer measurement possible.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JA1001). Services for accessing these data are described at the back of the journal.

## References

- Khan, F. A., Czerwonka, R., Zimmer, R. & Reissig, H.-U. (1997). *Synlett*, pp. 995–997.

- Nicolaou, K. C., Dai, W.-M. & Guy, R. K. (1994). *Angew. Chem. Int. Ed. Engl.* **33**, 15–44; *Angew. Chem.* **106**, 38–69.
- Sheldrick, G. M. (1991). *SHELXTL/PC. X-MOL. Interactive Molecular Graphics Program for Display of Crystal Structures*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997a). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997b). *SHELXS97. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.
- Stoe & Cie (1996). *XRED. Data Reduction Program*. Version 1.07. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1997). *STADI4. Diffractometer Control Program*. Version 1.06. Stoe & Cie, Darmstadt, Germany.
- Wani, M. C., Taylor, H. L., Wall, M. E., Coggon, P. & McPhail, A. T. (1971). *J. Am. Chem. Soc.* **93**, 2325–2357.

*Acta Cryst.* (1999). **C55**, 1943–1945

## 2,6-Dimethylspiro[1-oxa-2,5-diazabicyclo-[3.3.0]octane-3,1'-cyclohexane]-4,6-dione

DAMON R. BILLODEAUX,<sup>a</sup> FRANK R. FRONCZEK<sup>a</sup> AND YAŞAR DÜRÜST<sup>b</sup>

<sup>a</sup>Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA, and <sup>b</sup>Department of Chemistry, Kocaeli University, TR-41300, Izmit, Turkey. E-mail: fronz@chxray1.chem.lsu.edu

(Received 29 June 1999; accepted 26 July 1999)

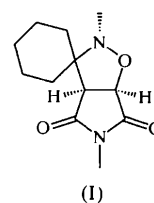
### Abstract

The title compound, C<sub>12</sub>H<sub>18</sub>N<sub>2</sub>O<sub>3</sub>, contains two fused five-membered rings; a nearly planar pyrrolidine ring, with a maximum deviation of 0.0352 (11) Å, and an oxazolidine ring in an envelope conformation. The average C=O distance of the pyrrolidine ketone groups is 1.210 (2) Å. The N—O distance in the oxadiazoline ring is 1.458 (2) Å. The structure contains a spiro-cyclohexane group in a chair conformation.

### Comment

The 1,3-dipolar cycloaddition of nitrones to different unsaturated systems has been the subject of extensive investigation since this method can be used to synthesize many heterocyclic compounds of great pharmaceutical importance, such as indolizine, quinolizine and indole alkaloids. A literature search revealed that few examples of cycloadditions of nitrones to reactive dipolarophiles, such as *N*-methyl- and *N*-phenylmaleimides, have appeared (Padwa, 1984; Torssel, 1988; Grünanger & Vita-Finzi, 1991; Cordero *et al.*, 1989, 1990; Brandi *et al.*, 1992; Goti, 1996). For this reason, the title cycloadduct, (I), was synthesized and its structure determined. Details

of the synthesis, chemistry and spectroscopy of (I) have been published elsewhere (Dürüst *et al.*, 1999).



The structure of (I) contains two fused five-membered rings, *i.e.* a 1,2-oxazolidine and an *N*-methylpyrrolidine ring (Fig. 1). The pyrrolidine ring system is nearly planar, with a maximum deviation of 0.0352 (11) Å for the C5 atom. The C=O bond lengths of the ketone groups are 1.210 (3) Å for C7=O9 and 1.210 (2) Å for C5=O10. The O9 atom is essentially coplanar with the ring, deviating by only 0.015 (3) Å, while O10 deviates by 0.102 (3) Å from the best-fit plane. The C16 *N*-methyl group has an N—C distance of 1.454 (3) Å and lies 0.061 (4) Å from the best plane.

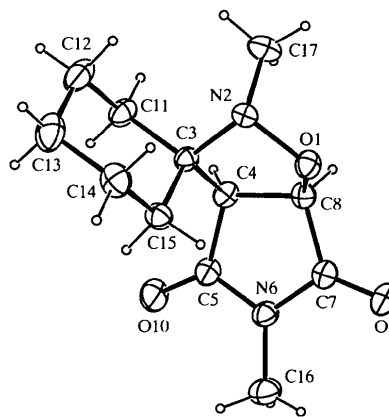


Fig. 1. ORTEP (Johnson, 1976) drawing of (I) with ellipsoids at the 50% probability level.

The oxazolidine system, by contrast, is a puckered ring. The ring has an envelope conformation with the N2 atom in the flap position and puckering parameters  $Q = 0.403$  Å and  $\varphi = 215.85^\circ$  (Cremer & Pople, 1975). The endocyclic torsion angle around C3—N2 is  $-40.1(2)^\circ$  and around N2—O1 is  $42.6(2)^\circ$ . The N—O bond distance in the ring is 1.458 (2) Å (N2—O1), which compares well with similar distances in previously reported structures (Grigg *et al.*, 1993; van Eijk *et al.*, 1988). The C17 *N*-methyl group has a C—N distance of 1.464 (3) Å and, along with the H atoms at C8 and C4, lies on the convex side of the bicyclic system, which also occurs in similar compounds (Grigg *et al.*, 1993).